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Trace metals in the suspended particulate matter of the Yellow River (Huanghe) Estuary: Concentrations, potential mobility, contamination assessment and the fluxes into the Bohai Sea

Xuelu Gao [a,b,*], Fengxia Zhou [a,c], Chen-Tung Arthur Chen [b], Qianguo Xing [a]

[a] Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, Shandong 264003, China
[b] Department of Oceanography, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan
[c] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Excessive input of trace metals contributes much to the degradation of many coastal ecosystems. As one of the most turbid large rivers in the world, the Yellow River, also called Huanghe, transports huge amounts of freshwater and suspended particulate matter (SPM) each year from its catchment as far as thousands of kilometers inland into the Bohai Sea, and has the most profound influence on the ecosystem of the Bohai Sea compared with other rivers that empty into it. In this research, the SPM were collected from the Yellow River Estuary twice in April and August, 2013. Six environmental quality assessment-related trace metals, namely Cd, Cr, Cu, Ni, Pb and Zn, were measured for their total concentrations and fractionations to understand their spatial and seasonal variations, potential mobility, pollution status and fluxes. The total concentrations of Cd, Cu and Pb in the wet season were very similar to their corresponding values in the dry season, while the total concentrations of Cr, Ni and Zn in the wet season were slightly higher than those in the dry season. The distributions of the studied metals in the geochemical fractions showed no notable spatial and seasonal variations. Except for Cd and Ni, the metals in the most labile fraction having the highest potential risk to biota on average accounted for $<2\%$ of their respective total concentrations; the percentages of Cd and Ni in this fraction were 54.5% and 10.1%, respectively. Anthropogenic influence on the spatial and seasonal variations of particulate Cr, Cu, Ni and Zn in total concentrations seemed weak and they were dominantly of natural sources. Results indicated that the Yellow River emptied about 0.0081×10^3, 2.11×10^3, 0.98×10^3, 1.10×10^3, 1.01×10^3 and 2.64×10^3 t a^{-1} of particulate Cd, Cr, Cu, Ni, Pb and Zn into the Sea, 86% of which happened in the wet season starting from June through October. These numbers were only 2.5–5.3% of the annual trace metals fluxes in the 1980s. One of the reasons for this was the reduction of SPM load; the fact that previous chemical fluxes data were measured at sites inland far from the mouth of the Yellow River was also responsible for this because a major proportion of SPM recorded at that site were deposited into the river bed during the transport between that site and the mouth of the Yellow River. Such a deposit actually did not reach the Bohai Sea, and probably had no direct influence on the environment and ecosystem of the Bohai Sea beyond the mouth of the Yellow River.

1. Introduction

China has been experiencing rapid economic development accompanied by large-scale environmental crises such as heavy smog and marine pollution especially into the 21st century. Many reports indicated that Chinese coastal marine environments have faced serious threats from massive human activities (e.g. Chen et al., 2007; Chang et al., 2012; Yuan et al., 2012; Yu et al., 2013; Gao et al., 2014). Coupled with various natural factors, the direct and possible consequences of anthropogenic effects on the coastal marine ecosystems in China are that the original ecological balance has been changed leading to the occurrence of ecological disasters such as the large-scale outbreaks of jellyfish, harmful algal blooms and green tides (e.g. Shen et al., 2011; Zhang et al., 2012; Xu et al., 2013; Xing et al., 2015).

Surrounded by the biggest economic rim in China, the shallow, semi-enclosed Bohai Sea has turned from an important fishing

* Corresponding author at: Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, Shandong 264003, China. Fax: +86 535 2109000.
E-mail address: xlgao@yic.ac.cn (X. Gao).

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ground to a heavily polluted sea, with the eco-environmental condition degrading significantly and the ecological functions declining rapidly in recent two decades (Xu, 2011; Pan and Wang, 2012; Gao et al., 2014). The concentrations of trace metals in sediments are important indicators reflecting the environmental quality of a marine area. Trace metals are naturally occurring substances and most of them are essential for living organisms. However, they become environmental toxicants when the concentrations exceed certain thresholds, and are non-biodegradable in the environment and easy to accumulate and magnify in organisms. Trace metals have been observed to be accumulating in sediments of many areas in the Bohai Sea, and their existence in high concentrations is potential threats to the biota (Gao et al., 2014).

The Bohai Sea is also a river-dominated ocean margin. Flowing through the biggest loess deposit area in the world, the Loess Plateau in the northern central China, the Yellow River (Huanghe) carries huge amounts of freshwater and suspended particulate matter (SPM) making it register as the most dominant land-based effect on the ecosystem of the Bohai Sea. With the amount of water discharged being far less than 1% of that of the Amazon River, the Yellow River transports enormous amounts of SPM being comparable to that of the Amazon River to the sea each year at its peak time in the 20th century, and tops the list of the world's most turbid rivers (Milliman and Ren, 1995). So, information about trace metals in the SPM of the Yellow River is helpful for a better understanding of the influence of the SPM discharge from the Yellow River on the trace metals in sediments of the Bohai Sea.

This work was conducted to study the concentrations and fractionations of six trace metals, i.e. Cd, Cr, Cu, Ni, Pb and Zn, in the SPM of the Yellow River Estuary (YRE), to evaluate their pollution status, to estimate their fluxes into the sea and then to give a synthetic judgment on whether the SPM of the Yellow River was a source for metal pollution in sediments of the Bohai Sea. Cd, Cr, Cu, Ni, Pb and Zn were studied because they are parameters widely used in environmental quality criteria (Gao and Chen, 2012; Gao and Li, 2012).

2. Materials and methods

2.1. Sampling

The field surveys in this study were carried out twice on April 26 and August 15, 2013, representing the condition of the dry season and the wet season, respectively.

The water samples were collected manually with acid-rinsed polyethylene bottles on a boat from 17 sites in April and 8 sites in August (Fig. 1). At each sampling site, 2 l of water were collected. The sampling depths were estimated to be 20–30 cm below the surface of the river. The sampling sites formed a transect extending from ~10 km in the lowermost estuary to ~10 km in the turbidity plume out of the mouth of the Yellow River (Fig. 1). After collection, the water samples were stored in a cooler box with ice packs and transported to the laboratory within 12 h.

2.2. Analytical methods

Once transferred to the laboratory, the water samples were filtered immediately. The SPM was recovered by filtration through

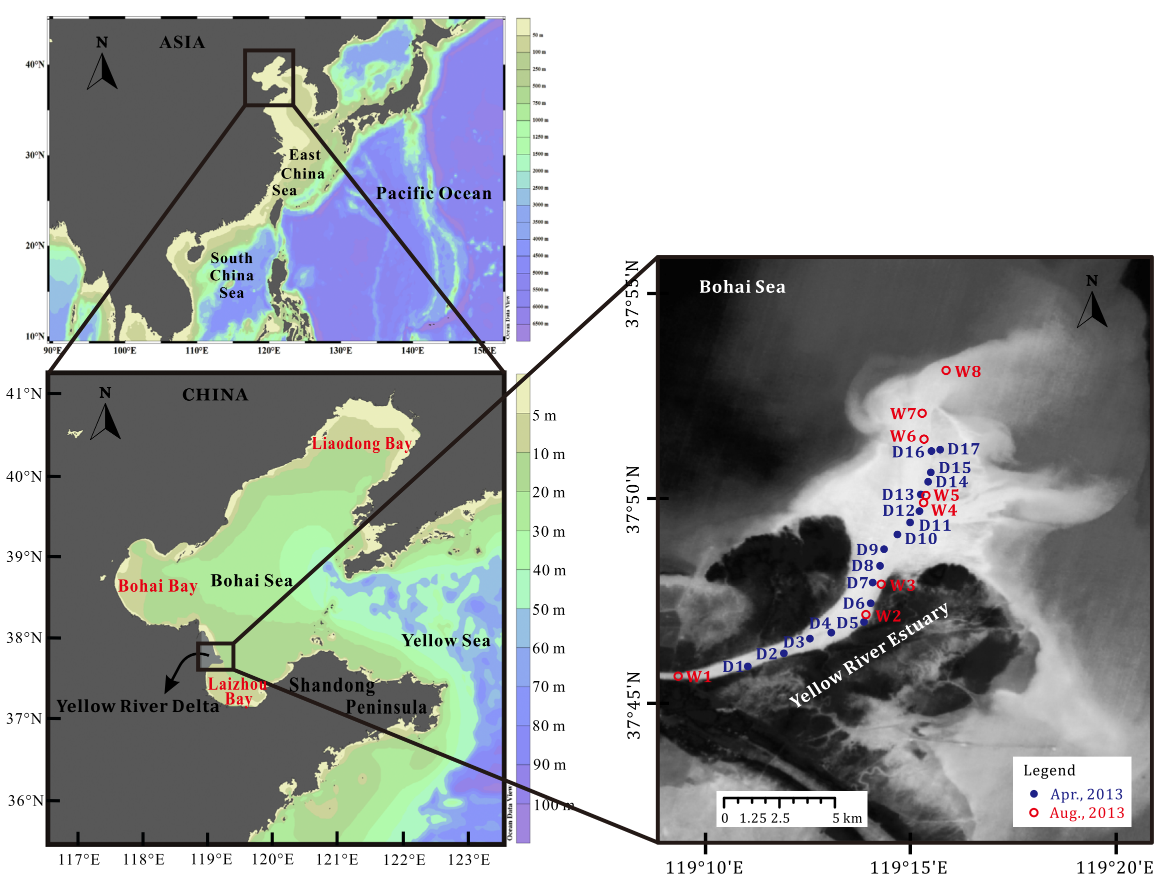

Fig. 1. Map of the Yellow River Estuary. It shows the sampling locations of the two cruises carried out in April (blue dots) and August (red hollow circles), 2013. The basemap in the right panel, which is the HJ-1 satellite image on August 15, 2013, clearly shows the turbidity plume (bright gray area) in the Yellow River Estuary (HJ-1 satellite image was provided by the China Centre for Resources Satellite Data and Application). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)